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PATENT SPECIFICATION

(11) 1 338 823

DRAWINGS ATTACHED

- (21) Application No. 2474/71 (22) Filed 19 Jan. 1971
 (31) Convention Application No. 4240 (32) Filed 20 Jan. 1970
 (31) Convention Application No. 72825 (32) Filed 16 Sept. 1970 in
 (33) United States of America (US)
 (44) Complete Specification published 28 Nov. 1973
 (51) International Classification C22C 11/02
 (52) Index at acceptance

C7A 740 781 783 B249 B279 B289 B309 B319 B339 B349
 B369 B389 B399 B419 B439 B44Y B451 B453
 B455 B459 B489 B519 B539 B549 B559 B610
 B613 B614 B619 B621 B624 B627 B62X B630
 B633 B634 B661 B663 B665 B667 B669 B66X
 B670

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(54) STABLE WROUGHT LEAD-CALCIUM AND LEAD-CALCIUM TIN ALLOYS

(71) We, ST. JOE MINERALS CORPORATION, a Corporation organised and existing under the laws of the State of New York, United States of America, having an office at 250 Park Avenue, New York, New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the production of wrought lead-calcium and lead-calcium-tin alloys which have tensile strength stability at room temperature and to alloys produced thereby.

Lead-containing alloys are useful in a variety of fields, such as in the construction of batteries. Alloys of lead, however, have physical properties which are somewhat deficient in regard to strength, strength stability at room temperature, heat stability and stress-rupture or creep resistance.

It is an object of the present invention to provide wrought alloys of lead having tensile strength stability at room temperature and, according to certain embodiments of the invention, having improved strength, heat stability and stress-rupture or creep resistance.

In general, the present invention provides stable wrought alloys of lead by casting a lead-containing alloy having a defined calcium content, and preferably defined relative and absolute tin contents, and thereafter working the casting within a defined limited time period after casting.

The time period between casting and working is essential in order to produce wrought lead-calcium alloys and wrought lead-calcium-

tin alloys which have tensile strength stability at room temperature, i.e., the wrought alloys of the invention have strengths which are either immediately stable at room temperature ("immediate stability") or which increase gradually with time up to 60—120 days or more and then become stable at room temperature ("long-range stability") as opposed to wrought alloys having strengths at room temperature which decrease with time either immediately or months after working. This time period between casting and working can be greater as the relative tin to calcium content is increased.

The tin to calcium weight ratio or relative tin content is important in order to produce wrought lead alloys not only having strength stability at room temperature but also having improved strength, heat stability and stress-rupture or creep resistance. These latter properties increase and then decrease as the tin to calcium weight ratio increases.

It is also important that the absolute tin content be regulated, particularly so as not to exceed a maximum value, in order to achieve strength stability at room temperature.

More specifically, the present invention provides a process for the preparation of a wrought alloy of lead having tensile strength stability at room temperature which comprises casting an alloy consisting of from 0.02% to 0.1% by weight of calcium and the balance substantially lead; and working the casting at room temperature at a time within 8 hours from casting. It is preferred that the alloys have a calcium content of from 0.06% to 0.09% by weight. Significant strengthening of the alloy can be achieved by adding tin in an amount such that the tin to calcium weight ratio or relative tin

content is from 5:1 to 10:1 and the absolute tin content is from 0.3% to 3.0% by weight and in this case working of the casting at room temperature must take place at a time within 48 hours from casting. It is preferred that the alloy contain tin in an amount such that the tin to calcium weight ratio or relative tin content is from more than 10:1 to 150:1 and preferably from 16:1 to 40:1 and the absolute tin content is from 0.3% to 3.0% by weight in which case working of the casting at room temperature must take place at a time within 7 days from casting. The absolute tin content is preferably from 0.6% to 2.0% by weight of the alloy. Most preferably the tin to calcium weight ratio is about 25:1.

The cast alloys are worked within a particular limited time period after casting, which time period can be increased as the relative tin to calcium content is increased. Thus, the tin-free lead-calcium alloys must be worked or deformed within 8 hours after casting. However, the tin-containing lead-calcium alloys having a tin to calcium weight ratio of from 5:1 to 10:1 can be worked or deformed within 48 hours after casting and the tin-containing lead-calcium alloys having a tin to calcium weight ratio of from more than 10:1 to 150:1 can be worked or deformed within 7 days after casting. Even with these two types of tin-containing lead-calcium alloys, however, it is preferred that they be worked or deformed within 8 hours after casting because of the superior properties obtained thereby.

Conventional batch or continuous metallurgical techniques can be employed in the casting and working operations of the process of the invention. Working can include such techniques as rolling, extruding, forging and the like.

The invention is described in more detail with reference to the accompanying drawings in which:

Figure 1 shows graphs of Ultimate Tensile Strength vs Aging Time (Room Temperature) for a Lead—0.08% Calcium (no Tin) Alloy;

Figure 2 shows graphs of Ultimate Tensile Strength vs Aging Time (Room Temperature) for a Lead—0.08% Calcium—0.5% Tin Alloy;

Figure 3 shows graphs of Ultimate Tensile Strength vs Aging Time (Room Temperature) for a Lead—0.08% Calcium—1.0% Tin Alloy;

Figures 4 and 5 show graphs of Ultimate Tensile Strength vs Aging Time (Room Temperature) for Lead 0.08% Calcium—0%, 0.5% and 1.0% Tin Alloy;

Figure 6 is a graph showing the effects of the Sn—Ca Weight Ratio on the Tensile Strength of Pb—Ca—Sn Alloy Rolled Sheet Aged 120 Days at Room Temperature;

Figure 7 shows graphs of the Effects of

Heat Treatment at 150°F on the Tensile Strength Properties of Rolled Sheet of Lead—0.07% or 0.08% Calcium—0%, 0.5% and 1.0% Tin Alloys.

Figure 8 shows a graph of the Effect of Tin Content on the Stress Rupture Properties of Lead—0.065% Calcium—Tin Alloy Rolled Sheet at a Stress of 3000 PSI.

In Figs. 1—8 of the drawings and in Table I below the casting and working operations were performed in the following manner. The lead component of the alloys was a corroding grade lead; the calcium component was commercial calcium having a purity of 99.5%; and the tin component, where used, was tin having a purity of 99.9%. The alloys were continuously cast on a pilot scale continuous caster. The cast slabs were 10½ inches wide and ½ inch or ¼ or ⅛ inch thick. In order to obtain satisfactory as-cast structures and surfaces, each thickness was cast at a different temperature, i.e., the ½ inch thick castings were made at a casting temperature of 700°F., the ¼ inch thick castings were made at a casting temperature of 725°F. and the ⅛ inch thick castings were made at a casting temperature of 750°F. The temperatures were held as closely as possible during casting, but crude temperature control permitted variations of as much as ±10°F. during the length of a cast. The alloys were cast at a rate of 3½ feet per minute.

The working operation was rolling. Thus, the continuously cast alloys were rolled to 0.040 inch using a constant rolling pass schedule, as follows: 0.750", 0.500", 0.350", 0.200", 0.120", 0.065" and 0.040". The starting material was a continuously cast strip 0.750" or 0.500" thick which was rolled to final gauge after aging at room temperature for varying time periods, namely, for 8 hours (Process A), 1 day (Process B), 7 days (Process C), 14 days (Process D) and 30 days (Process E). The behaviour of the rolled sheet was evaluated on the basis of heat stability, tensile strength and stress-rupture (an indirect measure of creep resistance) properties during aging at room temperature for up to 240 days or longer. The tensile strength was measured using ASTM standard 1" gauge length specimens and a testing speed of 0.5 inch/minute. The stress-rupture or creep resistance testing was performed with 2" gauge length specimens. All samples were prepared on a Tensile-Kut machine.

The effect and importance of the time period between casting and rolling on tensile strength and tensile strength stability at room temperature may be seen in Figs. 1, 2 and 3 for representative alloys, namely, a lead—0.08% calcium (no tin) alloy, a lead—0.08% calcium—0.5% tin alloy and a lead—0.08% calcium—1.0% tin alloy, respectively. The curves show the effect of rolling within 8 hours after casting (Process A), 1 day after

casting (Process B), 7 days after casting (Process C), 14 days after casting (Process D) and 30 days after casting (Process E). The data for the lead—0.08% calcium (no tin) alloy (Fig. 1) show that this tin-free material rolled within 8 hours after casting exhibits the lowest tensile strength level, but the tensile strength is immediately stable with time at room temperature ("immediate stability"). However, tin-free materials rolled 1, 7, 14 and 30 days after casting, although exhibiting initially higher tensile strength levels, nevertheless have tensile strengths which are not stable with time at room temperature; and after reaching a peak somewhere between 10 and 40 days, the tin-free materials produced by all of the other processes proceed to decrease in tensile strength. Tensile strength data taken after 240 days (not presented in Fig. 1) revealed that tin-free material processed by Process B and E became weaker than tin-free material manufactured in accordance with Process A and that the downward trend of Process C and D continued.

Fig. 2 likewise shows the effect of the time period between casting and rolling on tensile strength and tensile strength stability at room temperature of a lead—0.08% calcium—0.5% tin alloy fabricated in accordance with the same five Processes A—E. Here it may be seen that material having a tin to calcium weight ratio in the range from 5:1 to 10:1, e.g., 6.25:1, rolled within 8 hours after casting (Process A) and material rolled 1 day after casting (Process B) increase gradually in tensile strength at room temperature over a four-month period and subsequently level off ("long-range stability"). However, waiting 7, 14 and 30 days (Processes C, D and E, respectively) between casting and rolling yields materials which appear to increase in physical properties for approximately 60 days and then proceed to diminish in tensile strength at room temperature.

The relationship of tensile strength at room temperature as a function of time for a lead—0.08% calcium—1.0% tin alloy fabricated via Processes A, B, C and E is shown in Fig. 3. In this tin-containing alloy having a tin to calcium weight ratio in the range from more than 10:1 up to 150:1, e.g., 12.5:1, there was achieved by Processes A, B and C a stable tensile strength at room temperature ("long-range stability") which was higher than that for the tin-free alloy of Fig. 1. These data show that a delay of up to 7 days between casting and working by rolling does not result in decreasing properties,

although the shorter the time delay the stronger the alloy. However, waiting 30 days (Process E) before rolling yields a material which reaches a maximum tensile strength at room temperature considerably below the tensile strength resulting from the other processes and which decreases very slowly with time thereafter.

Fig. 4 shows the relatively orderly behavior as to "immediate stability" and "long-range stability" of the three alloys of Figs. 1, 2 and 3 cast under identical conditions and rolled within 8 hours after casting (Process A). It will be noted once again that the lead-calcium alloys containing tin had appreciably greater tensile strength at room temperature than did the lead-calcium alloy free of tin.

Fig. 5 shows the rather chaotic effect on tensile strength of the same three alloys of Figs. 1, 2 and 3 if 30 days (Process E) elapse between casting and rolling. A comparison of the curves for Figs. 4 and 5 shows the importance of working the lead-calcium and lead-calcium-tin alloys at a time period shortly after casting in order to achieve a stable tensile strength at room temperature.

Fig. 6 is a plot of the tin to calcium weight ratio versus the tensile strength at room temperature for various billet thicknesses of $\frac{1}{2}$ ", $\frac{3}{4}$ " and 1" of lead alloys containing between 0.06% and 0.09% calcium. This curve shows that the tin to calcium weight ratio or relative tin content is one of the key parameters of the process of the invention in determining maximum tensile strength at room temperature. These data show that, by using the tin to calcium weight ratio as the controlled variable, the scatter in properties due to variation in chemical composition and billet thickness disappears. Fig. 6, taken together with Table I below, demonstrate that the tin to calcium weight ratio or relative tin content should be from more than 10:1 up to 150:1 and that this ratio usually should be from 16:1 to 40:1 to maximize the tensile strength at room temperature of the aged wrought lead-calcium-tin alloys. This figure also shows that at a tin to calcium weight ratio of from 5:1 to 10:1 the tensile strength at room temperature of an aged wrought tin-containing lead-calcium alloy can be somewhat improved.

The data in Table I below give the ultimate tensile strength after aging periods up to one year at room temperature of various wrought lead-calcium-tin alloys produced by Process A wherein the relative and absolute tin contents were varied.

TABLE I

Example No.	Sn/Ca Weight Ratio	Weight Percent Sn	Weight Percent Ca	Ageing Time (Days)						
				1	7	14	30	60	120	365
1	24 : 1	2.00	.082	8300	1,200	10600	10600	10800	—	—
2	26 : 1	1.95	.074	7500	8600	—	9000	9500	10500	10500
3	27 : 1	1.17	.043	6100	6900	7300	8900	9300	—	—
4	33 : 1	1.81	.055	7950	9600	10200	10500	10500	—	—
5	40 : 1	2.72	.068	8000	8600	—	8800	8900	9100	9100
6	50 : 1	2.47	.049	8600	9900	—	10500	10500	—	—
7	61 : 1	1.29	.021	6500	6700	6800	7300	—	—	—
8	100 : 1	3.00	.030	—	—	—	—	—	—	—
9	148 : 1	2.52	.017	6700	6800	6900	7200	—	—	—
10	83 : 1	4.95	.055	9000	10300	10100	9600	8500	—	—
11	115 : 1	6.32	.055	9400	9900	7900	7200	6300	—	—

As pointed out above, the data in Table I, taken together with Fig. 6, illustrate the fact that the tin to calcium weight ratio or relative tin content should be from more than 10:1 up to 150:1 and that this ratio usually should be from 16:1 to 40:1 to maximize the tensile strength at room temperature of the aged wrought lead-calcium-tin alloys. The data for Examples 1—9 of the invention taken together with the data from the Process A curve in Figs. 2 and 4 compared with those for Examples 10 and 11 not within the scope of the invention (because the absolute tin content of the lead-calcium-tin alloys exceeded about 3.0% by weight) further illustrate or indicate that the absolute tin content should be from 0.3% to 3.0% and preferably from 0.6% to 2.0% by weight of the alloy in order further to achieve strength stability at room temperature. Furthermore, the data for Examples 1—3 wherein the tin to calcium weight ratio or relative tin content was substantially constant i.e. about 25:1, indicate that the strength of the wrought lead-calcium-tin alloys increases as the calcium and tin absolute contents increase.

The other facets of adding tin to lead-calcium alloys are shown in Figs. 7 and 8 which respectively establish that tin in a high amount increases the tensile strength stability of the system at elevated temperatures, such as 150°F., and dramatically improves the stress-rupture or creep resistance properties. Thus, in Fig. 7 the lead alloy having a tin to calcium high weight ratio in the range from more than 10:1 up to 150:1, e.g., 14.3:1, was substantially heat stable at the elevated temperature, whereas the other two lead alloys having low tin to calcium weight ratios of 6.25:1 and 0:1 (no tin) were not heat stable at the elevated temperature. From Fig. 8 it can be seen that the lead alloys having tin to calcium weight ratios of more than 10:1 and higher suffer rupture only after about 70 hours at a stress of 3000 psi. as contrasted with the tin-free lead-calcium alloy which ruptured after only a half hour of stress.

It will be noted that the abscissa for Figs. 1—7 is on a linear scale, whereas the abscissa for Fig. 8 is on a logarithmic scale.

WHAT WE CLAIM IS:—

1. A process for the preparation of a wrought alloy of lead having tensile strength stability at room temperature which comprises casting an alloy consisting of from 0.02% to 1.0% by weight of calcium and the balance substantially lead; and working the casting at room temperature at a time within 8 hours from casting.

2. A process as claimed in claim 1 wherein the alloy has a calcium content of from 0.06% to 0.09% by weight.

3. A process for the preparation of a wrought alloy of lead having tensile strength stability at room temperature which comprises casting an alloy consisting of from 0.02% to 0.1% by weight of calcium, tin in an amount such that the tin to calcium weight ratio is from 5:1 to 10:1 and the absolute tin content is from 0.3% to 3.0% by weight, and the balance substantially lead; and working the casting at room temperature at a time within 48 hours from casting.

4. A process as claimed in claim 3 wherein the alloy has a calcium content of from 0.06% to 0.90% by weight.

5. The process as claimed in claim 3 or 4 wherein the casting is worked at room temperature at a time within 8 hours from casting.

6. A process for the preparation of a wrought alloy of lead having tensile strength stability at room temperature which comprises casting an alloy consisting of from 0.02% to 0.1% by weight of calcium, tin in an amount such that the tin to calcium weight ratio is from more than 10:1 to 150:1 and the absolute tin content is from 0.3% to 3.0% by weight and the balance substantially lead; and working the casting at room temperature at a time within 7 days from casting.

7. A process as claimed in claim 6 wherein the alloy has a calcium content of from 0.06% to 0.09% by weight.

8. A process as claimed in claim 6 or 7 wherein the tin to calcium weight ratio is from 16:1 to 40:1 and the absolute tin content is from 0.6% to 2.0% by weight.

9. A process as claimed in claim 8 wherein the tin to calcium weight ratio is about 25:1.

10. A process as claimed in any of claims 6 to 9 wherein the casting is worked at room temperature at a time within 8 hours from casting.

11. A process for the preparation of a wrought alloy of lead having tensile strength stability at room temperature substantially as hereinbefore described.

12. A wrought alloy of lead having tensile strength stability at room temperature when prepared by a process as claimed in any of claims 1 to 11.

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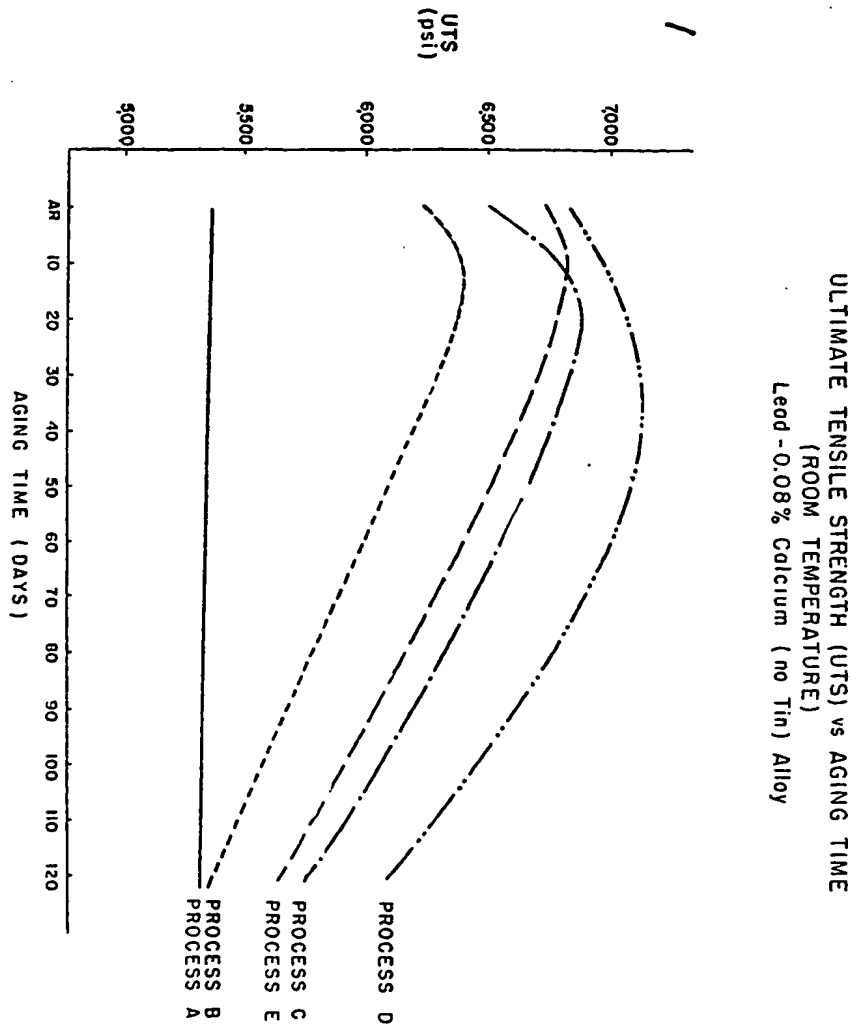
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FIG. 1



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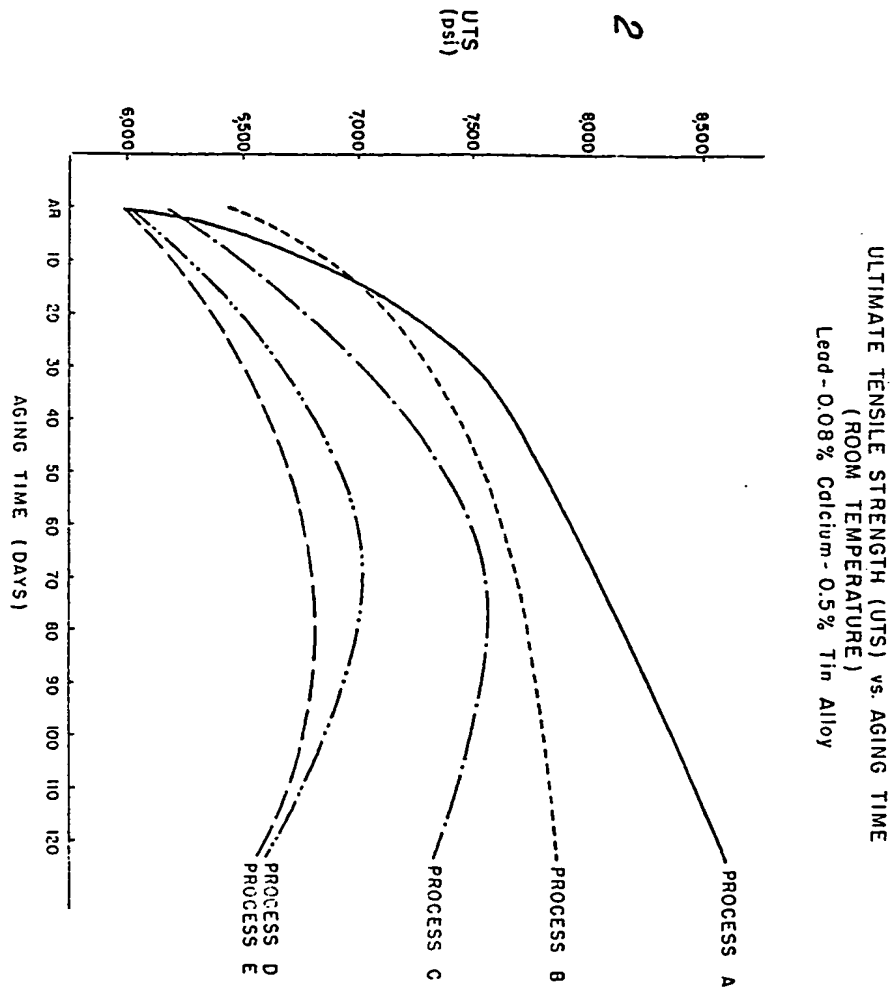
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FIG. 2



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FIG. 3

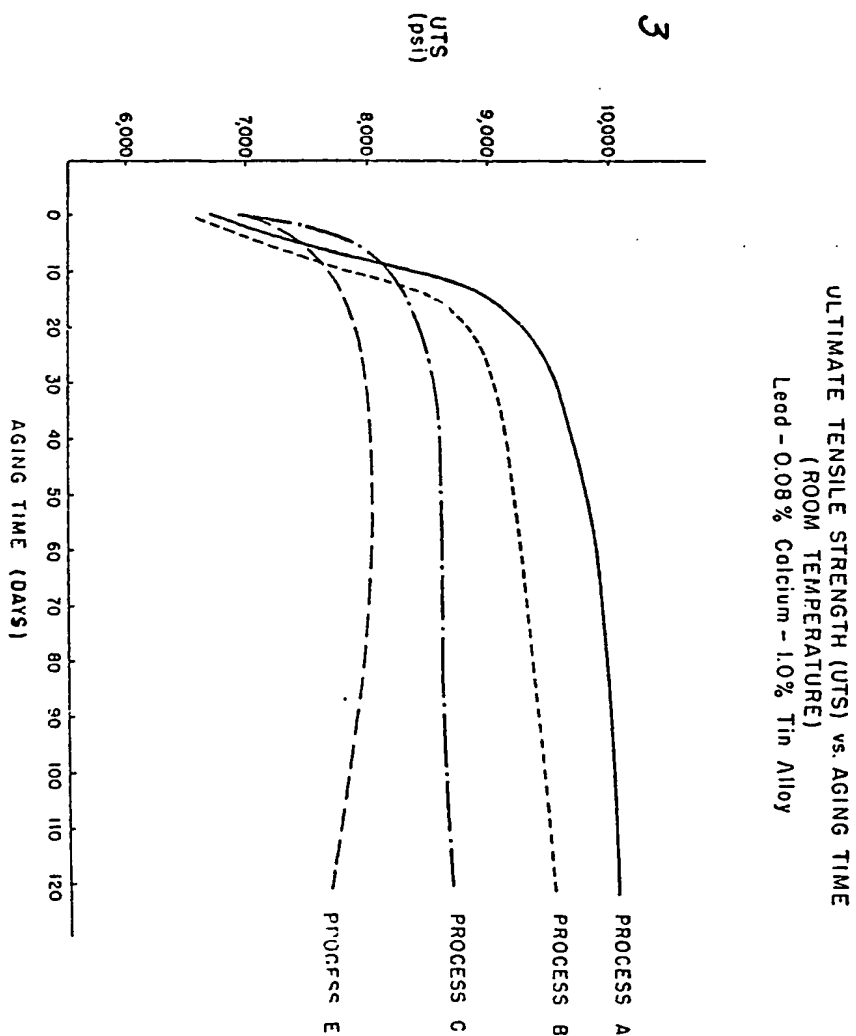
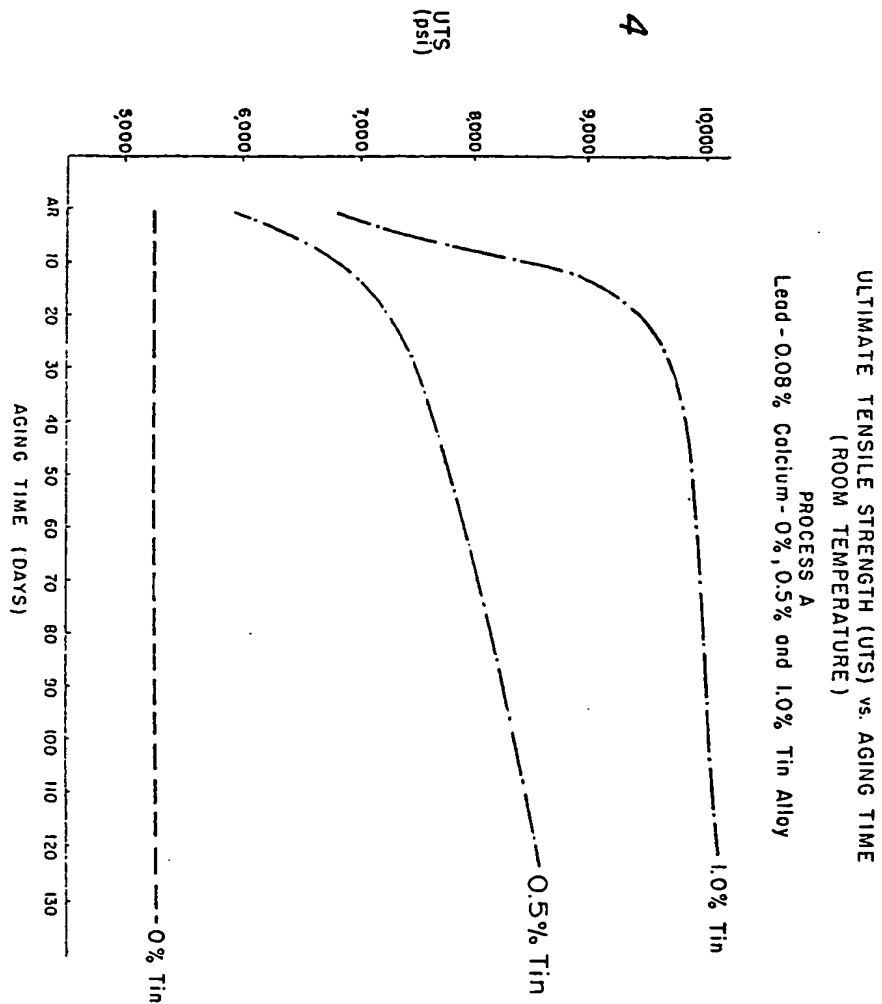


FIG. 4



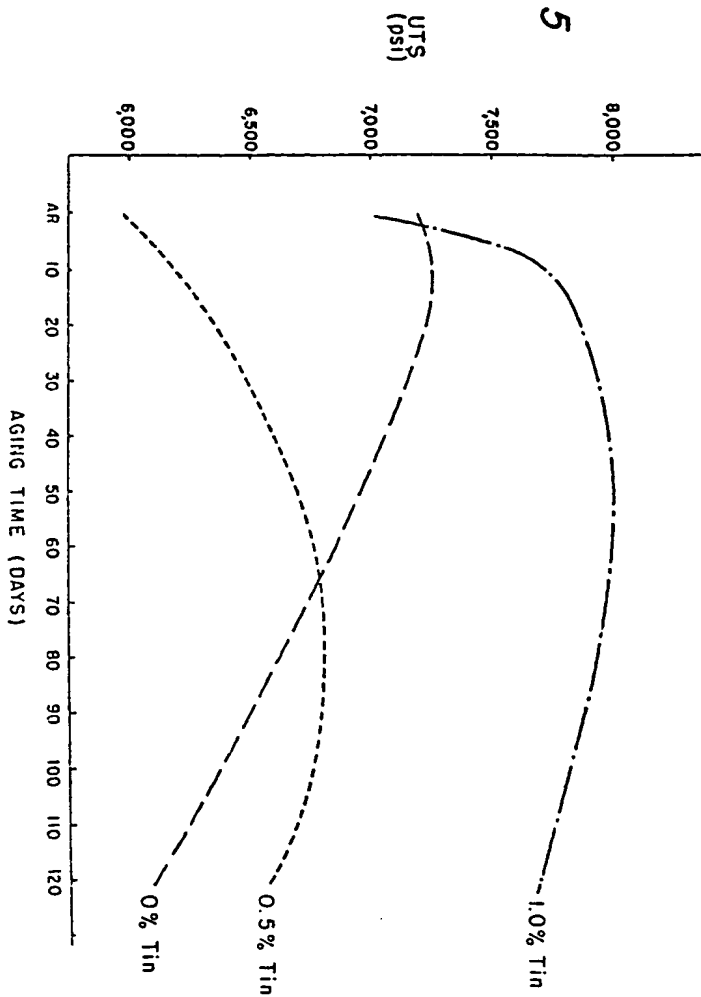
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FIG. 5



ULTIMATE TENSILE STRENGTH (UTS) vs. AGING TIME
(ROOM TEMPERATURE)

PROCESS E

Lead - 0.08% Calcium - 0%, 0.5% and 1.0% Tin Alloy

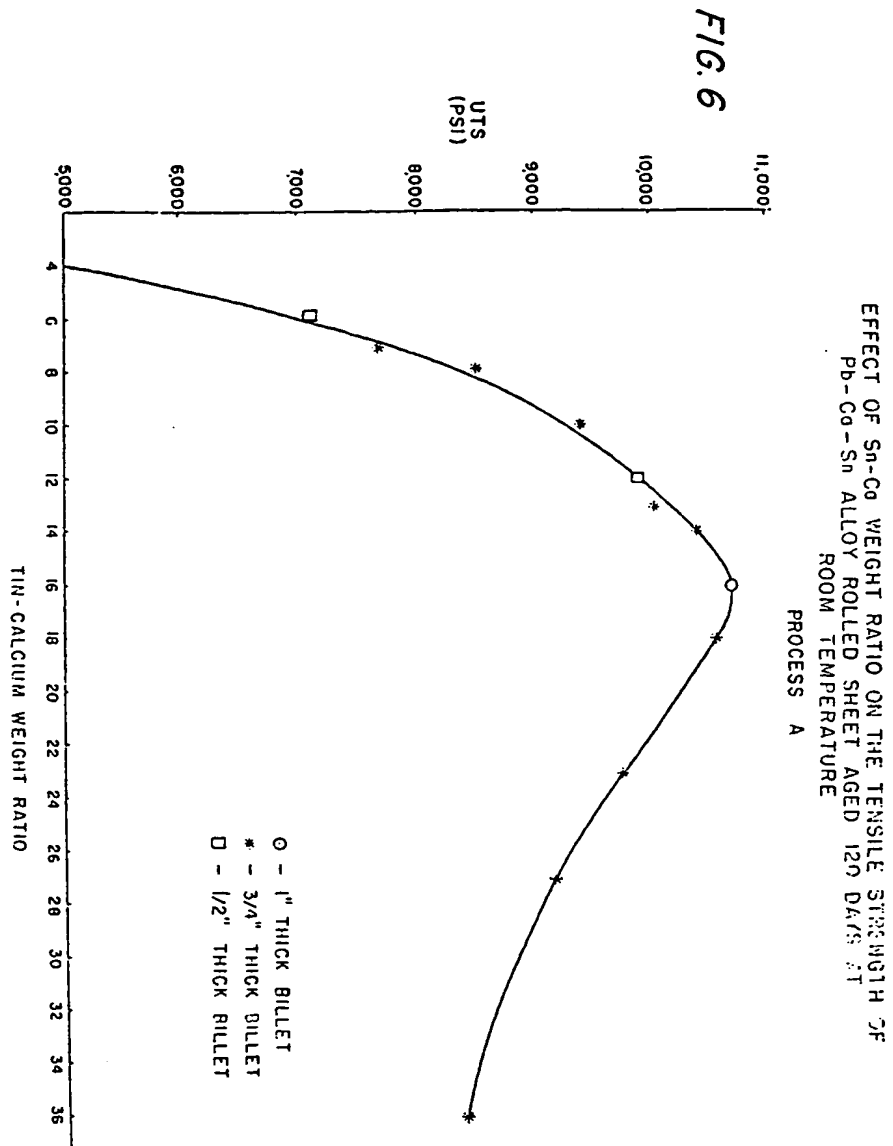
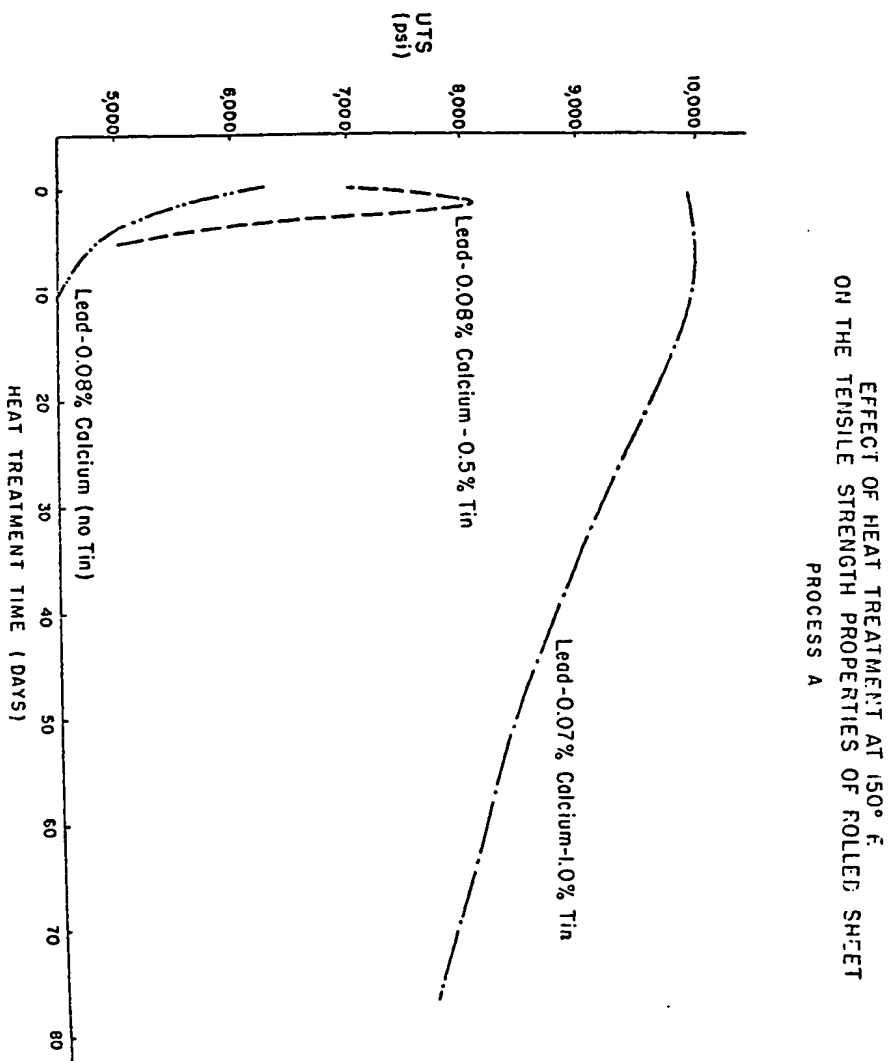


FIG. 7



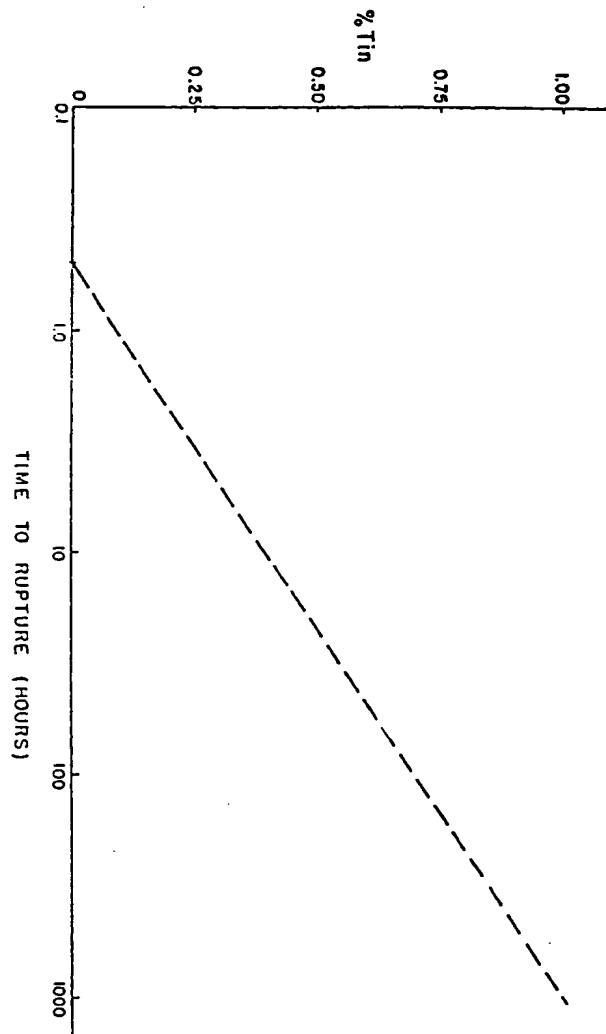
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FIG. 8



EFFECT OF TIN CONTENT ON THE STRESS-RUPTURE
PROPERTIES OF LEAD-0.065% CALCIUM-TIN
ALLOY ROLLED SHEET AT A STRESS OF 3000 PSI

PROCESS A

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